



# Selective leaching of copper and zinc from primary ores and secondary mineral residues using biogenic ammonia

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## ARTICLE INFO

Editor: Navid B Saleh

### Keywords:

Biohydrometallurgy

Ureolysis

Metal recovery

Tailings

Waste processing

## ABSTRACT

With the number of easily accessible ores depleting, alternate primary and secondary sources are required to meet the increasing demand of economically important metals. Whilst highly abundant, these materials are of lower grade with respect to traditional ores, thus highly selective and sustainable metal extraction technologies are needed to reduce processing costs. Here, we investigated the metal leaching potential of biogenic ammonia produced by a ureolytic strain of *Lysinibacillus sphaericus* on eight primary and secondary materials, comprised of mining and metallurgical residues, sludges and automotive shredder residues (ASR). For the majority of materials, moderate to high yields (30–70%) and very high selectivity (>97% against iron) of copper and zinc were obtained with 1 mol L<sup>-1</sup> total ammonia. Optimal leaching was achieved and further refined for the ASR in a two-step indirect leaching system with biogenic ammonia. Copper leaching was the result of local corrosion and differences in leaching against the synthetic (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> control could be accounted for by pH shifts from microbial metabolism, subsequently altering free NH<sub>3</sub> required for coordination. These results provide important findings for future sustainable metal recovery technologies from secondary materials.

## 1. Introduction

With the increased global demand for critical and economically important metals and the depletion of easily accessible ores, alternate metal sources are becoming of increased interest (European Commission, 2010, 2017). Secondary sources, such as mine tailings, metallurgical residues, sludges and automotive shredder residues, whilst often lower in metal concentration than primary ores, are highly abundant, thus present a promising solution to the critical metal crisis. Traditional hydrometallurgical techniques to acquire metals from primary ores typically use concentrated acids, bases or solvents, and while often can lead to selective and high leaching from primary ores, are hindered by high costs and poor sustainability from loss of lixiviant and/or production of further waste streams. Furthermore, selective metal extraction from secondary materials is also desirable to leave a cleaner residue that could be used for further valorisation, such as construction materials (Binnemans et al., 2015). Alternative leaching technologies that offer

high yields, selectivity and sustainability are thus needed for these lower grade mineral residues to become economically viable.

Biohydrometallurgy exploits microbial metabolisms for metal extraction through mineral separation via bioflotation (Sanwani et al., 2016) or metal extraction via autotrophic or heterotrophic bioleaching (Heitkamp and Orth, 1997; Potysz et al., 2018). Chemolithotrophic bioleaching involves direct iron/metal sulfide oxidation and metal dissolution from production of sulfuric acid and is currently applied on an industry scale for pure or polymetallic ores and tailings for Cu (contributing to 21% of global mining), Au, Ni, Co and Zn (Johnson, 2014). Heterotrophic bioleaching presents an alternate technology with broader applications towards non-sulfidic matrices that cannot be targeted by autotrophic pathways. Ex-situ production of a metal leaching/chelating biolixiviant followed by leaching in two step leaching modes also can alleviate the need for direct microbe-matrix contact, eliminating metal-microbe toxicity effects. Despite these clear advantages, heterotrophic bioleaching is yet to reach industrial scale. A

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<https://doi.org/10.1016/j.jhazmat.2020.123842>

Received 27 May 2020; Received in revised form 25 August 2020; Accepted 26 August 2020

Available online 3 September 2020

0304-3894/© 2020 The Author(s).

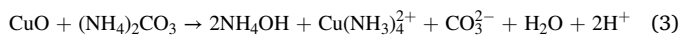
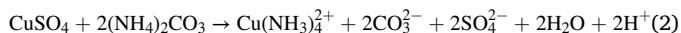
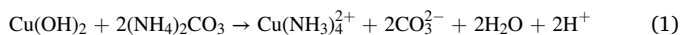
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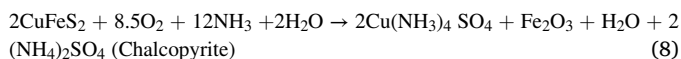
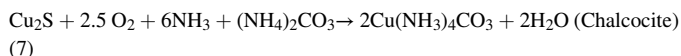
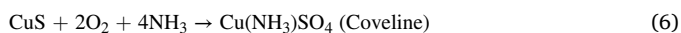
vast number of studies in heterotrophic bioleaching have focussed on bacterial (e.g. *Pseudomonas* sp.) or fungal (e.g. *Aspergillus*, *Penicillium* sp.), organic acid production to leach metals from primary ores (Valix and Usai, 2001; Maes et al., 2017), and secondary e-wastes (Brandl et al., 2001), slags (Potysz et al., 2018) and sludges (Pathak et al., 2009). While organic acids can be tuned to above their respective  $pK_a$  for metal chelation and stability, a trade off with proton attack at the material surface is lost which may inhibit its metal extraction potential.

Since the early 1900's, ammonia has been used in hydrometallurgy for a number of metals, including Cu, Zn, Ni, Co, Cd, Au and Ag (Meng and Han, 1996). It has advantages over other lixiviants due to low cost, ease of regeneration and high selectivity due to insolubility of typical competing metals such as Fe and Ca. Several ammoniacal species have been used to target different metal and mineral systems and it is often reported that ammonium carbonate is advantageous over other species due to its relative low toxicity and stability of free  $NH_3$  and the resulting metal ammine complex by carbonate (Jha et al., 2001; Zapp et al., 2012). Copper leaching of metals from solid matrices by ammonium carbonate is well documented. However, little is known about metal extraction with biogenic ammonia, with just two studies to date implicating the role of microbially produced ammonia from a low grade Cu ore (Wang et al., 2013; Hu et al., 2016). Moreover, no studies to date have investigated the use of biogenic ammonium carbonate with more complex and heterogeneous secondary mineral residues.

Leaching of Cu hydroxides, oxides and basic metal salts by ammonia do not require oxidative dissolution (1–3) (Wayne Richardson, 1997), while copper in metallic form requires an oxidative step, via  $O_2$  to  $CuO$  (4), or subsequently coordinated cupric ammine species (5) (Strmčnik et al., 2009).

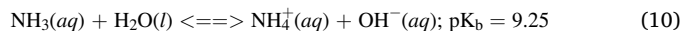
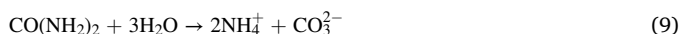


Hydrometallurgy studies using ammonia have also focussed on high temperature and pressures to optimise leaching of copper sulfides, which also requires an oxidative step to break the copper sulfide bond and liberate sulfate (6–8) (Yin et al., 2018).



Ammonium carbonate is also a potent leaching agent of zinc in oxide and sulfate forms, but poorly leaches from sulfide, silicate, ferrite or if bound in spinels such as franklinite (Harvey, 2006).

Biogenic ammonia in the environment is ubiquitous, produced from a diverse number of prokaryotic and eukaryotic organisms via ammonification, dissimilatory nitrate reduction to ammonium, or ureolysis (Kuypers et al., 2018). Urea is commonly found in domestic wastewaters as urine, contributing 9.3–23 g  $L^{-1}$  (Rose et al., 2015). With urea production surpassing 150 m t per year (Antonetti et al., 2017), it also is a major waste product from a diverse number of industries and environmental processes including fertiliser leachates (Urbańczyk et al., 2016; Gilbert et al., 2006). A diverse number of microorganisms possess the urease enzyme to convert urea into carbonate and ammonia (9) which partitions between  $NH_3$  and  $NH_4^+$  (10) (Mobley and Hausinger, 1989).



This study aims to determine the suitability of biogenic ammonia for extraction of economically important (Ni, Zn and Cu) metals from a diverse spectrum of primary and secondary materials. *Lysinibacillus spahericus* has been previously demonstrated to give high urea turnover yields over a wide pH range (pH 7–11) and in the presence of high metal concentrations (Wang et al., 2017), thus was selected in this study for optimal biogenic ammonia production. This study also intends to identify optimal leaching parameters and elucidate metal extraction mechanisms through modifications of contact times, leaching modes and physiochemical parameters. Together, this study will identify suitable ammoniacal leaching and material combinations that provides important first steps towards future sustainable metal recovery technologies.

## 2. Materials and methods

### 2.1. Materials and leaching experiments

Eight materials were tested in this study (SI Table 1). The first group (shredder residues and sludges) were comprised of a landfilled automotive shredder residue (ASR), a landfilled Cr-Ni neutralization sludge from stainless steel production and a Zn rich sludge from hazardous waste processing. The second (metallurgical residues) were sourced from a fayalitic slag from a zinc smelting plant, a CuS mine tailing and a landfilled Zn processing residue from the goethite process (Zn Fe residue). The third group (primary ores) that were tested were from a concentrated high grade ZnO ore and a low-grade Polish Ni laterite ore. All samples are representative of their respective origin and prior to leaching experiments were dried in a low temperature oven (40 °C). For (pseudo-) total metal content determinations, material digestions were conducted in triplicate using aqua regia digestions on 0.2 g of solid material. All subsequent leaching experiments were performed in triplicate, aside from the growth media control (singular), at 30 °C and 120 rpm. To limit particle size effects between leaching experiments, samples were crushed and sieved to below 1 mm. The exception to this was the particle size optimization experiment, where the ASR was sieved through successive sieves (1 mm, 0.5 mm, 0.2 mm, 0.1 mm) before mixing with 1 mol  $L^{-1}$  biogenic ammonia. A pulp density of 10% was used throughout this study, aside from pulp density optimization experiments where 5%, 2.5% and 1.25% of the ASR was mixed with 1 mol  $L^{-1}$  biogenic ammonia. Leaching experiments with higher pulp densities (>10%) were not possible as it impeded adequate mixing.

For the initial screening experiments, two step ammoniacal leaching was performed by mixing synthetic  $(NH_4)_2CO_3$  (Sigma Aldrich, Belgium) or biogenic ammonia (Section 2.2) at a total ammonia concentration of 1 mol  $L^{-1}$  with each material for a contact time of 24 h. For the subsequent selection of leaching mode, one step biogenic ammonia and two step biogenic and synthetic leaching experiments (Section 2.2) were conducted with the ASR over a contact time of 1 week. A repeat two step batch leaching experiment involved successive leaching of the same ASR material with fresh 1 mol  $L^{-1}$  total biogenic ammonia. Separation of the material and the leachate was performed via centrifugation after each leaching step before the addition of fresh lixiviant. To investigate the impact of biomass during two step leaching, biogenic ammonia was either mixed with the ASR directly (lixiviant + cells), or filtered using a 0.22  $\mu m$  filter prior to leaching (lixiviant – cells). To determine if any other metabolic byproducts influenced leaching, biogenic ammonia was stripped from the culture media by heating to 50 °C for one week under a ventilation hood. The residual ammonia free solution was then readjusted to its original volume with  $dH_2O$  prior to the leaching experiment with the ASR. An additional control experiment (urea free media) with the ASR was performed by growing *L. spahericus* in 20 g  $L^{-1}$  yeast extract with no added urea, then separating the biomass via centrifugation before mixing the biolixiviant with the ASR. To assess the impact of different ammonia species on copper leaching from the

ASR, leaching experiments were conducted with pure synthetic ammonia compounds of 1 mol L<sup>-1</sup> NH<sub>4</sub>OH, 1 mol L<sup>-1</sup> NH<sub>4</sub>Cl or 0.5 mol L<sup>-1</sup> (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> (Sigma Aldrich, Belgium). To determine the impact of pH on ammoniacal copper leaching from the ASR, lixiviants were generated from mixtures of NH<sub>4</sub>HCO<sub>3</sub> and NH<sub>4</sub>OH at a total ammonia concentration of 1 mol L<sup>-1</sup> to give a pH of 8.8, 9, 9.2 and 9.5.

The selectivity index (S) was calculated by  $S (\%) = ((R_i - R_r)/R_i) \times 100$ .  $R_i$  is the recovery of the metals of interest (Cu, Zn or Ni), calculated by mass of metals of interest in output divided by input.  $R_r$  is the recovery of the residual fraction, which for simplicity was identified as iron; the highest competing metal common across all materials. Separation factors for each material were calculated as a ratio between each element in the leachate following the initial screening experiment with 1 mol L<sup>-1</sup> total synthetic and biogenic ammonia.

## 2.2. Culturing of *Lysinibacillus sphaericus*

*Lysinibacillus sphaericus* LMG22257 (Belgian coordinated collection of microorganisms, Ghent) was grown aerobically in Erlenmeyer flasks from glycerol stocks at 30 °C. Flasks were supplied with 20 g L<sup>-1</sup> yeast extract (Carl Roth, Germany) to promote optimal growth, similar to previous work with this strain (Wang et al., 2017), aside from experiments varying yeast extract concentration, where 10, 5, 2.5, 1.25 and 0.625 g L<sup>-1</sup> yeast extract was used. Urea (Sigma Aldrich, Belgium) was added to give 1 mol L<sup>-1</sup> total biogenic ammonia, aside from experiments varying biogenic ammonia concentration, where higher urea loadings were required to account for lower urea turnover yields (above 0.5 mol L<sup>-1</sup> urea).

A one step leaching experiment with the ASR involved mixing the ASR material with  $0.5 \times 10^8$  cells of *L. sphaericus* in its growth media to allow the theoretical in-situ production of 1 mol L<sup>-1</sup> total biogenic ammonia. All other experiments were conducted in a two-step manner, where biogenic ammonia was first produced by *L. sphaericus*, then separated from the residual biomass before mixing with the respective material. No difference in leaching was observed when cells were separated from biogenic ammonia by centrifugation or 0.22 µm filtration, thus centrifugation was chosen as a practical method for cell separation throughout this study. All two-step leaching experiments with biogenic ammonia were conducted within one day of its production.

## 2.3. Geochemical analyses and modelling

The pH was measured using a Consort multiparameter analyser C3020. Ammonia was determined using the Berthelot reaction (Bucur et al., 2006), followed by spectrophotometric quantification at 695 nm on a Tecan infinite plate reader. Organic acid production (acetic, propionic, butyric, citric, oxalic, gluconic, succinic) was assessed using high-performance liquid chromatography (HPLC, Ultimate 3000, Dionex, Germany). The HPLC was fitted with a resex ROA-organic acid H<sup>+</sup> column (Phenomenex, CA, USA) in a thermostatted column compartment TCC-100 at 60 °C with UV detection set to 210 nm by an UltiMate 3000 RS diode array detector. Samples were loaded via an UltiMate 3000 autosampler compartment and eluted with 5 mmol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> at a flow rate of 0.6 mL min<sup>-1</sup>. Anion analysis (PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup>) was performed using a 930 Compact IC Flex (Metrohm, Switzerland) equipped with chemical suppression and a conductivity detector. An eluent of 1.0 mmol L<sup>-1</sup> NaHCO<sub>3</sub> – 3.2 mmol L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> was used on a Metrosep A Supp 5–150/4.0 column and Metrosep A Supp 4/5 Guard/4.0 guard column. Analysis was performed using MagIC Net 3.1 software. Total digestions and ammoniacal leachates were filtered and diluted in 1% HNO<sub>3</sub> prior to analysis by Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES, Varian Vista MPX, US) for Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn and Ca. Throughout, the NH<sub>4</sub>:NH<sub>3</sub> partitioning ratio was calculated using  $NH_3 = ((NH_4^+ + NH_3) - 10^{pH})/e^{6344/273+T} + 10^{pH}$ . Thermodynamic modelling of Cu-ammonia equilibria as function of pH and Cu concentration, and

ammonium-ammonia speciation in NH<sub>3</sub>CO<sub>3</sub>H : NH<sub>4</sub>OH mixtures with varying pH was performed using the software OLI systems (v.10) applying the AQ database. Eh-pH diagrams of Cu and Zn were used to rationalize the leaching behavior in the experimental conditions and were calculated with the chemical equilibrium diagram software Hydra/Medusa.

## 2.4. Mineralogical analyses

All samples for X-ray powder diffraction (XRD) analysis were performed on unsieved, ground material (SI methods). The surface morphology of the automotive shredder residue was examined by a Jeol JSM-7600 field emission scanning electron microscope (FE-SEM). The shredded material was applied as a thin layer on a double-sided carbon tape and stuck on the sample holder. An energy dispersive X-ray spectrometer (EDX) attached to the FE-SEM was used for element mapping of the electron images. The FE-SEM micrographs were acquired in the secondary electron imaging mode (SEI) at an accelerating voltage of 15 kV and 8.0 mm effective working distance. The overview and magnified inset images were made at 50 times and 1000 magnifications respectively.

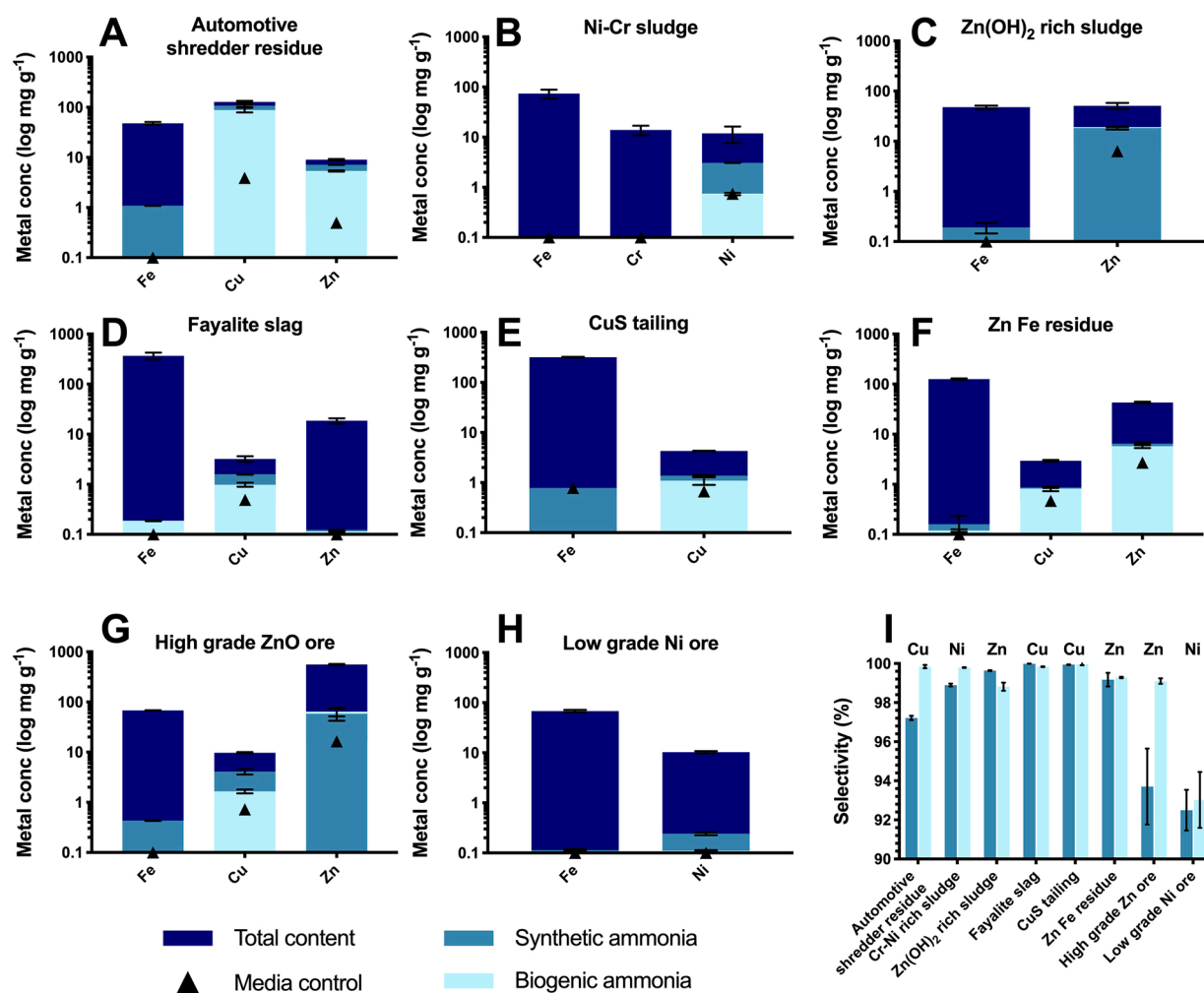
## 3. Results and discussion

### 3.1. Material screening

To identify which material sources could be suitable for leaching with ammonia, a preliminary screen of eight primary and secondary materials was performed with both synthetic and biogenic ammonia poised at a total ammonia concentration of 1 mol L<sup>-1</sup>. After a contact time of 24 h, target metals Cu, Zn or Ni generally dominated in the pregnant solution (Fig. 1, SI Table 1 and 2). To predict the leaching behaviour of Cu and Zn in ammoniacal solutions, Eh-pH diagrams were calculated and highlighted the thermodynamic feasibility of Cu(I), Cu (II) and Zn(II) amines under these experimental conditions that buffered between pH 8.8–9.8 (SI Fig. 1 and 2). The observed differences between materials was thus likely a result of the variable target metal bearing mineralogy (SI Fig. 3).

With respect to copper, a similar extent of leaching was observed for both biogenic and synthetic ammonia from the Zn(OH)<sub>2</sub> rich sludge (35–38%), the CuS tailing (26–32%) and the Zn Fe residue (28–29%), where Cu was in hydroxide, sulfide or sulfate form respectively (Fig. 1C, 1E, 1 F, SI Fig. 3 and SI Table 1). The highest copper extraction yields were measured for the ASR material, the fayalite slag and the high grade ZnO ore, reaching  $81 \pm 5\%$ ,  $(108 \pm 6 \text{ mg g}^{-1})$ ,  $49 \pm 1\%$  ( $1.57 \pm 0.02 \text{ mg g}^{-1}$ ) and  $42 \pm 5\%$  ( $4.09 \pm 0.5 \text{ mg g}^{-1}$ ) Cu, respectively (Fig. 1A, 1D, 1G). Interestingly, synthetic ammonia was more proficient over the biogenic form for these materials, where Cu was present primarily as Cu(0) or CuO (SI Table 1, SI Fig. 3), that are highly susceptible to (oxidative) dissolution (Radmehr et al., 2013). Evidently, for materials bearing Cu (0), the solubilisation of metallic copper will involve the prior electrochemical oxidation by oxygen or Cu (II) ions.

For zinc, synthetic and biogenic ammonia leaching largely matched each other across all materials (Fig. 1, SI Table 2). Optimal leaching of Zn was again observed from the ASR (60–80%), followed by the Zn (OH)<sub>2</sub> rich sludge (36–38%) (Fig. 1A and 1C). Whilst a relatively high concentration of Zn was obtained from the high grade ZnO ore (58–64 mg g<sup>-1</sup>), it represented a low recovery yield (10–12%) (Fig. 1G). Poor leaching yields from the fayalite (0.6%) and the Zn Fe residue at (13–15%) may be a result of Zn in inaccessible forms to ammonium carbonate leaching such as silicate (e.g. willemite) or spinel bound (e.g. franklinite) (Harvey, 2006), the primary forms of these metals in these materials (Fig. 1D and F, SI Table 1, SI Fig. 3). These results are consistent with previous study of ammoniacal leaching on a crude ZnO ore (Yang et al., 2019), although further mineralogical analyses on post leached materials are needed to support these hypotheses.



**Fig. 1.** Bioleaching screen of shredder and sludges (A–C), metallurgical residues (D–F) and primary ores (G+H) sieved at 1 mm and pulp density of 10% using biogenic (light blue) or synthetic (mid blue)  $(\text{NH}_4)_2\text{CO}_3$  at a total ammonia concentration of  $1 \text{ mol L}^{-1}$  in a two-step leaching mode and contact time of 24 h. Dark blue bars denote total metal content determined by aqua regia and black triangles signify leaching with growth media components only. Metal leaching is expressed logarithmically as the amount of metal extracted in mg, per g of material added. The average value and standard deviation of  $N = 3$  replicates is plotted, except for the media components only ( $N = 1$ ). Selectivity indices calculations (materials and methods) are presented for both synthetic and biogenic ammonia leaching as the metal of interest against iron for all materials tested (I). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Lower yields of nickel were observed compared to copper and zinc despite Ni amines having a similar thermodynamic feasibility to Cu and Zn (Meng and Han, 1996). Interestingly, the biological system (Fig. 1B:  $26 \pm 0.1\%$ ,  $3.1 \pm 0.01 \text{ mg g}^{-1}$ ) outperformed the chemical system for the Ni-Cr sludge (Fig. 1B:  $6 \pm 0.3\%$ ,  $0.73 \pm 0.05 \text{ mg g}^{-1}$ ). Poor leaching of the low grade Ni ore by both synthetic and biogenic ammonium carbonate was observed (Fig. 1H:  $2 \pm 0.1\%$ ,  $0.24 \pm 0.02 \text{ mg g}^{-1}$ ). Cross correlation between these mineral compositions indicated that Ni could be partially leached from trevorite phases, but not from silicate spinel minerals forsterite and willemseite (SI Table 1, SI Fig. 3). Typically, laterites are roasted prior to ammonia treatment (Caron process), but additional flotation and magnetic separation steps render this process expensive (Simate and Ndlovu, 2010).

Selectivity is also an important parameter to determine the success of a (bio)leaching technology. Iron was present in significant amounts in all the starting materials tested, at 5–35 wt % (SI Table 1), therefore selectivity indices were initially calculated for specific target metals against iron. Aside from the low grade Ni ore (93%), biogenic ammonia had a very high selectivity (>99%) of target metals against iron. Moreover, biogenic ammonia had a marked increase in selectivity over its synthetic counterpart for the ASR and the high-grade Zn ore,

increasing by 3 and 5% respectively (Fig. 1I). It is noteworthy that the pH of the synthetic  $(\text{NH}_4)_2\text{CO}_3$  leachate was at  $\sim 0.15$  units higher for all materials, except the ASR and the high grade ZnO ore, which was 0.6 and 0.9 units higher, respectively (SI Fig. 2). The lower pH in the biogenic ammonia leachates could be explained through the prior fermentation processes of the yeast extract and/or  $\text{CO}_2$  liberation via microbial respiration during ureolysis that improved its buffering capacity upon material contact. No organic acids were detected by HPLC during the growth of *L. sphaericus*, although other uncharacterised metabolic by-products cannot be ruled out.

To further explore selectivity of target metals with other elements, separation factors were calculated between all elements for each material with synthetic and biogenic ammonia (SI Table 3). Biogenic and synthetic ammonia were also highly selective against all other non-target metals tested. Although Co and Cr form hexa- or tetra-amine complexes, they are poorly soluble at the pH measured in these experiments, thus no measurable value ( $<0.1\%$ ) was observed in the leachates of all materials tested in the screen. Mn is also widely reported to be poorly soluble in ammoniacal solutions (Radmehr et al., 2013). Whilst Pb can be leached by ammoniacal solutions, subsequent reprecipitation is often observed, likely as  $\text{PbCO}_3$  or  $\text{PbSO}_4$  (Lim et al., 2013; Rudnik et al.,



2016). Interestingly, Cu leaching by biogenic ammonia was also more selective against Al compared to synthetic ammonia for the ASR and the high-grade Zn ore, corroborating the selectivity indices against Fe and thus may represent a similar cause of origin. When target metals Cu, Zn and Ni were co-occurring in a material, the preference for Cu, Zn or Ni generally correlated with its relative concentration in the material. The exception to this was for the fayalite material, where copper was preferentially extracted over the higher abundant zinc, supporting the previous hypothesis that ammonium carbonate is a poor leaching agent of metals from spinel phases.

To further characterise the composition of the synthetic and biogenic ammonia leachates for downstream processing considerations, analysis of key anions ( $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ ) was performed. Phosphate and nitrate were  $\sim 2 \text{ mmol L}^{-1}$  and  $\sim 3 \text{ mmol L}^{-1}$  respectively in the biogenic lixiviant, but dropped below detection limit ( $<0.1 \mu\text{mol L}^{-1}$ ) post leaching. Chloride was initially low ( $<0.3 \text{ mmol L}^{-1}$ ) and largely remained below  $0.3 \text{ mmol L}^{-1}$ , except for the  $\text{Zn(OH)}_2$  rich sludge ( $3.4 \text{ mmol L}^{-1}$ ), which matched the media control leachate. Sulfate was also initially low ( $\sim 2 \text{ mmol L}^{-1}$ ) but increased significantly in the Zn Fe residue and Ni-Cr sludge leachate at  $100\text{--}112 \text{ mmol L}^{-1}$  and  $138\text{--}163 \text{ mmol L}^{-1}$  respectively. Moderate sulfate leaching was observed from the high grade ZnO ore and CuS tailing, but was similar to the media control leachate. Sulfate remained below  $5 \text{ mmol L}^{-1}$  in all other materials (SI Fig. 4). Overall, based on total target metal yield and high selectivity against non-target cations and anions, the ASR was chosen for further experiments to optimise leaching modes and physiochemical parameters. Furthermore, mechanistic insights through biotic and abiotic matrix modifications and mineralogical analysis were required to resolve the marked differences in metal leaching between biogenic and synthetic ammonia to collectively infer insights to the original screen.

### 3.2. Characterisation of the ASR leaching process

Industrial bioleaching can be achieved via heap leaching in a one step process or stirred batch reactors either in one step or in a two-step spent leachate system. Hence, to give further insights into which technology could be suitable for biogenic ammonia leaching, a series of

direct one step and indirect two step leaching experiments were conducted with *L. sphaericus* and the ASR, sieved to  $<1 \text{ mm}$  and at a pulp density of 10%. In order to further characterise Cu, Zn and Fe extraction, multiple samples were taken over a longer contact time of 7 days (Fig. 2).

For the two step leaching experiment with  $1 \text{ mol L}^{-1}$  total biogenic or synthetic ammonia, a similar extent of leaching was observed to the original screen, but the higher resolution sampling identified that near maximum Cu leaching was achieved after only 4 h at  $86.1 \pm 5.8$  (65% of total Cu) and  $96.1 \pm 7.4 \text{ mg g}^{-1}$  (72% of the total Cu) with biogenic and synthetic ammonia, respectively (Fig. 2A). However, incomplete copper extraction was still observed despite the longer contact times. Thermodynamic modelling of the system highlighted that there was excess complexing agent and the copper amine complex has not reached its solubility product (SI Fig. 5). Subsequent 24 h two-step leaching with fresh  $1 \text{ mol L}^{-1}$  total biogenic ammonia on the same ASR material showed that higher leaching yields could be obtained through addition of new lixiviant, with essentially complete extraction of copper by the third transfer of biogenic ammonia (SI Figure 6). The additional extraction could thus be driven by the lower concentration of copper ions in the subsequent leaching reaction rather than an excess of free ammonia. Alternately, these observations could be the result of an initial decrease of pH (from 9.2 to 9) upon addition of fresh lixiviant, favouring dissolution of the Cu-oxide species of the passive film on the surface of metallic Cu particles (Strmcnik et al., 2009).

For zinc, similar initial biogenic and synthetic ammonia leaching was observed after 1 h ( $5.40 \pm 0.26$  and  $5.46 \pm 0.1 \text{ mg g}^{-1}$ , 60% of the total Zn) but increased to  $7.60 \pm 0.1 \text{ mg g}^{-1}$  in the chemical system (85% of the total Zn) after 48 h. A significant drop in Zn was observed by the end of the experiment (after 168 h), particularly in the synthetic ammonia leachate (Fig. 2B), where a pH rise to pH 9.8 was observed. Given the  $\text{Zn(NH}_3)_2^{2+}$  predominance area (pH 8.5–10) is slightly narrower in comparison to Cu amines (pH 8–10.5) (SI Fig. 1), the synthetic ammonia leachate approaches this boundary and thus may represent a reprecipitation of ZnO. Alternately it could be a result of Zn(II) adsorption to residual phases.

For iron, both biogenic and synthetic ammonia leached  $0.11 \pm 0.01$

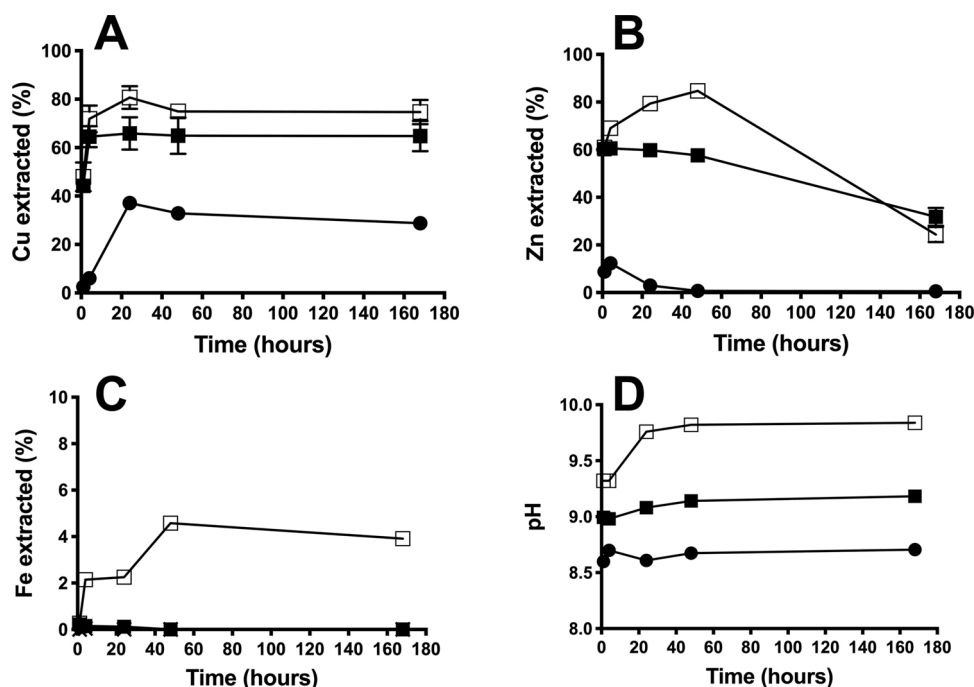


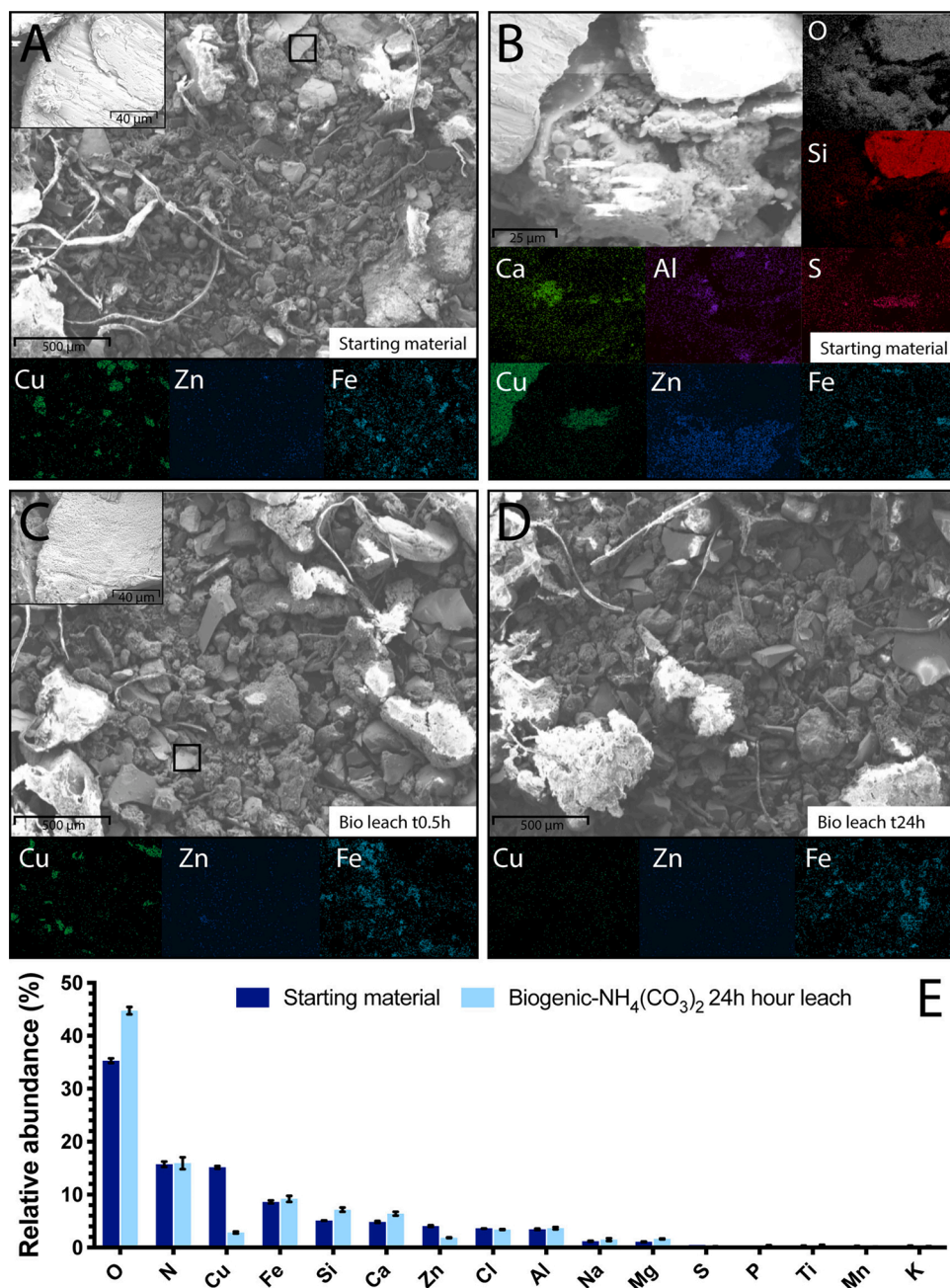
Fig. 2. One-step (●) vs two-step biological (■) and synthetic (□) leaching of *L. sphaericus* using  $1 \text{ mol L}^{-1}$  total biogenic ammonia with the automotive shredder residue a pulp density of 10% over a contact time of 7 days. The average value and standard deviation of  $N = 3$  replicates is plotted as a percentage of Cu (A), Zn (B), Fe (C) extracted relative to the start material, and the pH (D). Where not shown, errors are within the size of the symbol.

$\text{mg g}^{-1}$  and  $0.13 \pm 0.01 \text{ mg g}^{-1}$  after 1 h, but a significant increase to  $2.2 \pm 0.01 \text{ mg g}^{-1}$  (4.5% of total Fe) after 48 h was measured in the synthetic ammonia leachate. In the presence of oxygen, soluble ferrous ammine complexes in ammoniacal solutions are subject to oxidative precipitation as a variety of Fe(III) minerals (Klocke and Hixson, 1972). This agrees with the transient soluble iron concentrations in the biogenic ammonia system, however it is currently unclear why residual iron remained in the synthetic ammonia leachate. The measurable increase in pH across all treatments, particularly in the less buffered synthetic ammonia system could be attributed to the consumption of protons and production of hydroxide associated with ammonia mediated corrosion and complexation of copper (Fig. 2D). Alternately, it could also represent the loss of carbonate from the system via reprecipitation of other metal carbonates.

To support the hypothesis that copper leaching was occurring via corrosion of metallic Cu(0), SEM imaging was performed on the starting ASR material and after a contact time of 0.5 h and 24 h with  $1 \text{ mol L}^{-1}$

total biogenic ammonia (Fig. 3). At the initial timepoint, copper primarily existed as metallic copper (Fig. 3A and B) and Zn could be seen as smaller amorphous deposits scattered across the material, possibly present as oxides and/or incorporated into other mineral phases such as franklinite (Fig. 3B). After 0.5 h of leaching, extensive surface pitting of the Cu particles could be seen (Fig. 3C), indicating that local corrosion is the likely driver of copper leaching from this material by ammonia. Pitting corrosion is a type of local corrosion on passive surface films and the formation of passive copper films in neutral and basic solutions is well documented (Feng et al., 1997). After one day of leaching, EDX mapping and relative abundances confirmed significant Cu and Zn leaching had occurred in comparison with other major elements, supporting previous observations. It also highlighted that the bulk matrix remained largely unchanged and provided estimated abundances of Ca (~5%), Si (~5%), Na (~1%) and Mg (~1%) that were similar before and after leaching (Fig. 3D and E).

To explore the potential for one-step heap leaching application,



**Fig. 3.** SEM and EDX mapping for the starting automotive shredder residue material sieved <1 mm (A + B), and biologically leached material using  $1 \text{ mol L}^{-1}$  total biogenic ammonia in a two-step bioleaching mode at a pulp density of 10% with a contact time of 0.5 (C) and 24 (D) h. Black squares highlight locations of inset images at higher magnification to show copper surface morphology. Quantitative EDX analysis is presented as the average value and standard deviation of  $N = 3$  replicates (as mapping results from three separate images randomly chosen across the sample) of the starting material and following a 24 h leach using  $1 \text{ mol L}^{-1}$  total biogenic ammonia (E).

*L. sphaericus* was grown in direct contact with the ASR to produce a theoretical biogenic ammonia concentration of  $1 \text{ mol L}^{-1}$ . A comparison of total ammonia production by *L. sphaericus* in the presence or absence of the ASR showed clear inhibition of the material and/or metal leachate against this strain, with ammonia only reaching a maximum of  $78.8 \pm 5 \text{ mmol L}^{-1}$  (13% of a growth experiment performed in the absence of the ASR) at a pH of 8.6 (Fig. 2D, SI Fig. 7). A lower rate and extent of copper and zinc leaching was observed compared to the two-step leaching experiment, with a maximum yield of 37% ( $49 \pm 3 \text{ mg g}^{-1}$ ) Cu (Fig. 2A) and 12% ( $1.1 \pm 0.1 \text{ mg g}^{-1}$ ) Zn. Iron extraction was low (0.2%) and again transient, giving a high selectivity coefficient ( $>99.6\%$ ).

### 3.3. Biogenic and synthetic ammonia leaching mechanisms

To ascertain whether biotic factors were driving differences in copper leaching from the ASR, a series of two-step leaching experiments were first performed on the ASR at a contact time of 24 h with and without biomass (Fig. 4A). No difference in leaching with  $1 \text{ mol L}^{-1}$  total biogenic ammonia was observed if cells were present in the lixiviant, or if they were removed via centrifugation prior to leaching. No significant leaching was also observed when centrifuged biomass ( $2 \times 10^8$ ) cells were resuspended in  $\text{dH}_2\text{O}$  and reacted with the ASR. These results indicate no added effect of microbial contact with the material, but also importantly, that insignificant metal biosorption was occurring, alleviating the need for cell filtration steps prior to leaching.

To identify whether other biogenic compounds aside from ammonia were independently influencing copper leaching, leaching experiments were performed using a lixiviant produced after stripping biogenic ammonia from the culture broth post ureolysis (ammonia stripped), or after 48 h of growth on a media comprised solely of  $20 \text{ g L}^{-1}$  yeast extract (urea free media). Again, no significant leaching of copper was observed, highlighting that if any fermentation products of yeast extract were being produced, they had no direct impact on copper extraction. These results highlight that differences between biogenic and synthetic ammonia were of abiotic origin.

To investigate the role of pH and counterions on leaching, two-step leaching experiments were also performed with the ASR at a pulp density of 10% and a contact time of 24 h with different species of synthetic ammonium compounds normalised to  $1 \text{ mol L}^{-1}$  total ammonia. A significant reduction in leaching was observed for ammonium chloride and

hydroxide, extracting only  $16 \pm 2\%$  and  $23 \pm 1\%$  of the total copper respectively (Fig. 4B). Poor Cu leaching with  $\text{NH}_4\text{Cl}$  could be attributed to the low partitioning of  $\text{NH}_3$  ( $\sim 4\%$ ) for Cu complexation at pH 7.7 (SI Fig. 8). For  $\text{NH}_4\text{OH}$ , where the pH was above 11,  $\text{NH}_3$  partitioning is 100%, thus poor leaching was likely due to either unfavourable high pH reactivity with the shredder material, instability of ammonia (and loss via volatilisation) and/or stability of solid phase  $\text{Cu}(\text{OH})_2$  (Grujicic and Pesic, 2005). To further understand the impact of pH on Cu leaching, the ASR was mixed with combinations of  $\text{NH}_4\text{HCO}_3$  :  $\text{NH}_4\text{OH}$  at a total ammonia concentration of  $1 \text{ mol L}^{-1}$  to give a final pH of 8.8–9.3 (where theoretical free  $\text{NH}_3$  almost doubles from 34% to 62%). A near two fold increase in Cu extraction from  $40 \pm 1\%$  to  $59 \pm 3\%$  and  $71 \pm 0.1\%$  was observed for pH 8.8, 9.0 and 9.3, respectively (Fig. 4B and SI Fig. 8). Overall, these experiments highlight the link between pH, free  $\text{NH}_3$  and ligand on the leaching of copper from this material.

### 3.4. Optimising two step copper leaching

To optimise parameters for two step copper leaching of the ASR with  $1 \text{ mol L}^{-1}$  total biogenic ammonia, physiochemical (pulp density and particle size) and growth (media components urea and yeast extract) components were varied (Fig. 5). Decreasing pulp density from 10% to 2.5 wt% reduced copper leaching to  $19 \pm 1\%$  (Fig. 5A). This outcome contrasts with the observations reported in many bioleaching studies, where a decrease in pulp density typically results in higher extraction yields (Guo et al., 2010; Panda et al., 2015). Sieving the maximum particle size from 1 mm to 0.1 mm resulted in an increase in copper extraction to  $83 \pm 0.1\%$  ( $110 \pm 0.2 \text{ mg g}^{-1}$ ), which could either be a result of a larger volume: surface area ratio of the smaller copper particles, or an up-concentration of Cu particles through sieving (Fig. 5B). For the oxidative solubilisation of elements in their metallic state, the rate determining step is oxygen transport to the metal surface (Rudnik et al., 2016). The total rate of dissolution is independent of volume, and directly proportional to surface area, thus in agreement with our findings that more material and a larger surface area leads to a higher degree of corrosion and leaching (Halpern, 1953).

To determine the most cost-effective conditions for bioleaching and identify feasibility towards domestic wastewaters that will house lower nutrients and urea concentrations, several biogenic ammonia lixiviants were produced at a range of different total ammonia and yeast extract concentrations (Fig. 5C and D). Total biogenic ammonia concentrations

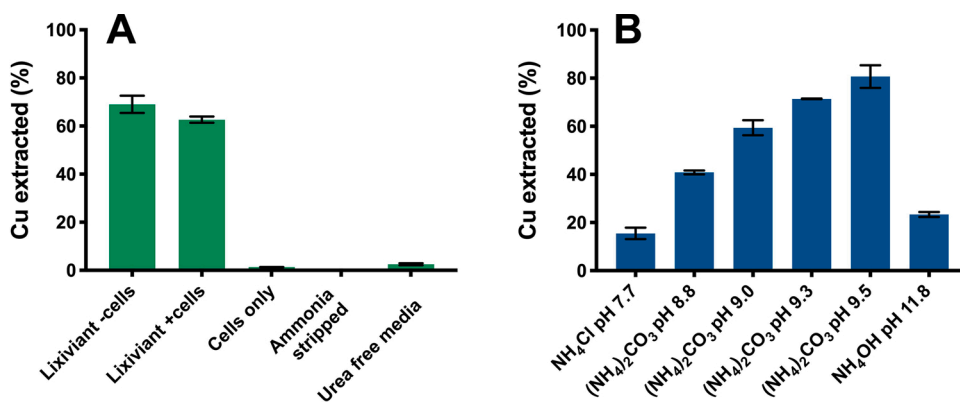


Fig. 4. Identifying biotic (A) and abiotic (B) parameters that impact two step ammoniacal copper leaching from the ASR. Biotic factors were explored during two step leaching with  $1 \text{ mol L}^{-1}$  biogenic ammonia in the presence of cell biomass (lixiviant + cells) or after removal via  $0.22 \mu\text{M}$  filtration (lixiviant – cells). Separated cells were subsequently resuspended in  $\text{dH}_2\text{O}$  and mixed with the ASR material (cells only). To identify whether other non-ammonia components of the biolixiviant were involved in copper extraction, ammonia was stripped post bioproduction prior to mixing with the ASR (ammonia stripped) and urea was omitted from the original culture media to give a non-ammonia bearing lixiviant (urea free media). Abiotic factors (ammonia speciation and pH) were assessed by using different synthetic ammonia species on copper leaching from the ASR using  $1 \text{ mol L}^{-1}$  total ammonia.  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  were added as pure solutions, whilst for pH modifications,  $\text{NH}_4\text{HCO}_3$  was mixed with  $\text{NH}_4\text{OH}$  to create a pH range of 8.8–9.3. The average value and standard deviation of  $N = 3$  replicates is plotted as a percentage of the copper extracted relative to the start material.



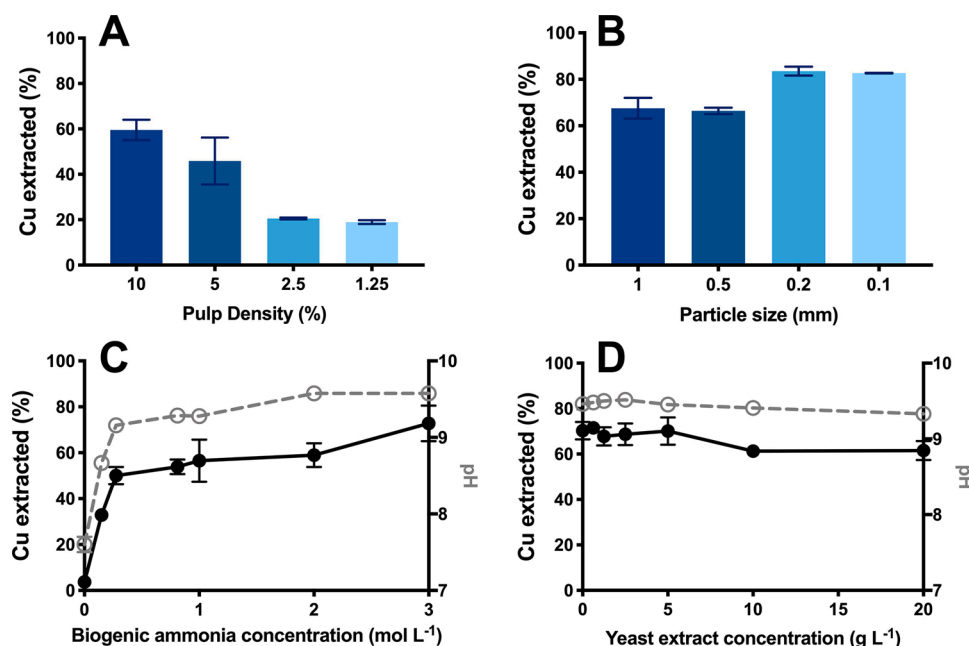


Fig. 5. Optimisation of physiochemical parameters: pulp density (A) and particle size (B) and media components: urea (C) and yeast extract (D) concentrations during two-step biogenic ammonia leaching of the automotive shredder residue at a contact time of 24 h. Grey dashed lines in C and D represent the pH of each sample. The average value and standard deviation of  $N = 3$  replicates is plotted as a percentage of the copper extracted relative to the start material. Where not shown, errors are within the size of the symbol.

were varied by adjusting the amount of urea in the growth media. Ureolysis yields were  $\sim 90\%$  up to  $0.6 \text{ mol L}^{-1}$  urea, but decreased to  $\sim 50\%$  at  $3 \text{ mol L}^{-1}$  urea, consistent with previous work (Wang et al., 2017). Essentially maximum leaching was obtained at  $0.275 \text{ mol L}^{-1}$  with biogenic ammonia (Fig. 5C), with a lower upward trend towards  $3 \text{ mol L}^{-1}$  total ammonia, but within analytical error limits. At lower total biogenic ammonia concentrations ( $<0.275 \text{ mol L}^{-1}$ ), decreasing copper extraction yields were observed. This could be a result of substrate limitation and the subsequent pH drop to 9.16 and 8.67 for 0.275 and  $0.15 \text{ mol L}^{-1}$  ammonia, thus reducing theoretical  $\text{NH}_3$  content to 54 and 27% respectively, negatively impacting Cu complexation. Whilst yeast extract is required for the initial robust growth of *L. sphaericus*, subsequent transfer into media containing  $0\text{--}20 \text{ g L}^{-1}$  yeast extract showed no impact on the production of  $1 \text{ mol L}^{-1}$  total ammonia. Interestingly, at lower yeast extract media concentrations, higher pH values were observed and a notable increase in the amount of Cu leached, reaching a maximum of  $72 \pm 3\%$  ( $95.6 \pm 3.8 \text{ mg g}^{-1}$ ) at  $0.625 \text{ g L}^{-1}$  yeast extract and a pH of 9.5 (Fig. 5D). This result confirms that enhanced buffering through biodegradation of the added yeast extract was the cause of the lower pH compared to synthetic ammonia, subsequently leading to the reduction in free  $\text{NH}_3$  for Cu coordination. Fortuitously, from an economic perspective, using higher loadings of material per volume and lower yeast extract concentrations is clearly advantageous.

#### 4. Conclusions and future application

This study presents a greener approach to Cu and Zn recovery, using both a more sustainable lixiviant production pathway and source of metals compared to traditional hydrometallurgy. It also provides the first comprehensive data set on ammoniacal leaching of metals from low grade mineral residues, which presents a number of important advantages over other current (bio)hydrometallurgical leaching technologies. (1) High yields and selectivity of Cu and Zn against the bulk matrix are well suited to leaching of heterogeneous lower grade materials, reducing downstream processing costs and facilitate the regeneration and reuse of the lixiviant. (2) The active lixiviant, biogenic ammonia, can be produced by *L. sphaericus* in high concentrations and yield from urea, a major component of domestic wastewaters, thus offers potential to couple two abundant sources of waste streams. Ammonium carbonate

outperforms typical ammonia products in industrial wastewaters (hydroxide, chloride) through a balance of pH and free ammonia for metal coordination. *L. sphaericus* also exhibits a tolerance to metals, pH and nutrient limitation, highlighting this strain as a suitable candidate for future biotechnological application.

This technology is particular beneficial in a two-step leaching mode for materials that contain low to mid-range concentrations ( $<10 \text{ wt } \%$ ) of CuO/ZnO and Cu(O)/Zn(O) particles ( $<1 \text{ mm}$ ) which are not suitable for traditional physical separation methods. Ammonium carbonate is likely not as effective for metals bound in recalcitrant spinel (e.g. silicate/trevorite) matrices however, typical for fayalite slags and laterite ores. Pre-treatment of these materials to weaken these phases could allow further downstream leaching with biogenic ammonia. The relatively low leaching efficiencies of the copper sulfide tailing in this study could be due to the ambient conditions used during leaching, thus further work could investigate elevated temperatures and pressures; however, this would reduce its sustainability.

It is estimated that  $0.5 \text{ m t}$  of automotive shredder materials are landfilled each year (Gent et al., 2015). While density separation processing adds further costs, the up-concentration of fine particulate metals will reduce the required volumes of lixiviant. At  $1 \text{ mm}$ ,  $13 \text{ wt } \%$  Cu and  $0.9 \text{ wt } \%$  Zn could provide a maximum of  $\text{€}210 \text{ m}$  per year. Leaching at a  $10 \text{ } \%$  pulp density would require a maximum of  $5 \text{ m t}$  lixiviant, costing a minimum of  $\text{€}20 \text{ m}$  (urea) or  $\text{€}23 \text{ m}$  (ammonium carbonate), respectively, assuming no recovery and reuse of the leaching agent. Whilst yeast extract is not necessary for ureolysis, it will help to provide essential nutrients for cell growth and viability, thus will further increase costs of biogenic leaching. *L. sphaericus* can also grow on a number of alternate carbon sources including acetate (Massie et al., 1985), which could reduce these processing costs. Sourcing urea as a waste stream, from e.g. urine that houses similar concentrations of urea to that used in this study would thus clearly be economically advantageous over using synthetic ammonium carbonate. Complete ureolysis of urine has recently been demonstrated at reactor scale (Christiaens et al., 2019), thus coupling these technologies has clear potential.

If 2-step bioreactors are unfeasible, in-situ heap leaching approaches could be investigated. Despite the lower predicted leaching turnovers in one step leaching, in-situ heap leaching approaches offer a relatively simple and economical engineering solution that could be applied to



existing tailing heaps. This could be particularly advantageous for mineral residues bearing lower metal concentrations, which would both reduce metal toxicity and require lower ammonia loadings. Whilst biofouling of industrial open bioreactors can be overwhelming, the high ammonia concentrations ( $>0.2 \text{ mol L}^{-1}$ ), alkaline pH ( $>9$ ) and subsequent extracted metal provide unfavorable conditions for competing nitrogen assimilation, nitrification or denitrification pathways (Ruiz et al., 2003; Hu et al., 2004). Future studies should focus on integrating ammonia reclamation (steam stripping), metal recovery ((bio)sorption) and/or emerging electrochemical technologies (Harvey, 2006; Bilal et al., 2013; Zhang et al., 2012), followed by scaling up and implementation in a semi-batch/continuous mode. Overall, this study shows promise for application towards the valorisation of solid and liquid industrial effluents which has implications for the transition towards a circular and bio-based economy.

#### CRediT authorship contribution statement

**Adam J. Williamson:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing - original draft, Writing - review & editing. **Florian Verbruggen:** Formal analysis, Investigation, Methodology, Writing - review & editing. **Vania S. Chavez Rico:** Data curation, Formal analysis. **Jef Bergmans:** Data curation, Formal analysis, Writing - review & editing. **Jeroen Spooren:** Formal analysis, Resources, Writing - review & editing. **Lourdes Yurramendi:** Formal analysis, Resources, Writing - review & editing. **Gijs Du Laing:** Funding acquisition, Resources, Writing - review & editing. **Nico Boon:** Conceptualization, Funding acquisition, Supervision, Writing - review & editing. **Tom Hennebel:** Conceptualization, Funding acquisition, Supervision, Formal analysis, Investigation, Writing - review & editing.

#### Declaration of Competing Interest

The authors reported no declarations of interest.

#### Acknowledgments

This work was conducted under the financial support of the Strategic Initiative Materials in Flanders (SIM) (SBO-SMART: Sustainable Metal Extraction from Tailings, grant no. HBC.2016.0456) and the European Union's Horizon 2020 research and innovation programme, Metal Recovery from Low-Grade Ores and Wastes Plus (METGROW+, grant no. 690088). FV acknowledges support by the Flemish Agency for Innovation and Entrepreneurship (Vlaio) via a Baekeland PhD fellowship (HBC.2017.0224) and by the Research & Development Umicore Group. We would like to thank Pieter Ostermeyer and Karel Folens for assistance with thermodynamic modelling and CMET and ECOCHEM group members and SMART/METGROW+ partners for valuable discussions throughout the project.

#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jhazmat.2020.123842>.

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